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**Henry's Law Constants for 2-Azidoethanamine Hypergols:
Estimates From a Density Functional Theory
/Polarizable Continuum Model**

by Michael J. McQuaid

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Henry's law constants at 298 K [HLC(298)] for four 2-azidoethanamine (EA) hypergols and three aliphatic amines were estimated via a density functional theory/polarizable continuum model (DFT/PCM) method. The four EAs are 2-azido-N,N-dimethylethanamine (DMAZ), 2-azido-N-methylethanamine (MMAZ), 1-(2-azidoethyl)pyrrolidine (PyrrAZ), and 4-(2-azidoethyl)morpholine (MorphAZ), and the three aliphatic amines are dimethylamine, trimethylamine, and 1-methyl-pyrrolidine. The estimates for the three aliphatic amines are all within a factor of 5 of measured values that have been reported for them, but all are somewhat low. The DFT/PCM-based estimate for DMAZ is about a factor of 2 smaller than an estimate obtained for it from the Environmental Protection Agency's HENRYWIN program and thus supports the reasonableness of the HENRYWIN estimate. In percentage terms, the DFT/PCM-based estimates for MMAZ, PyrrAZ, and MorphAZ are all significantly lower than those obtained from HENRYWIN, but the estimates from both methods suggest that the volatilization of these compounds from water will be negligible. Taken together, the results indicate that HENRYWIN's HLC(298) predictions for EA hypergols merit use as input for modeling their transport through the environment.					
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1. Introduction

Various 2-azidoethanamines (EAs) have demonstrated potential as fuels for hypergolic rocket propulsion systems (Thompson et al., 1998; Stevenson et al., 2004; McQuaid, 2006), and as part of an effort to determine whether candidates from this class warrant further testing and development, data that can be used to assess the risks they pose to human health and the environment are being generated and reported with support from an Environmental Quality Technology (EQT) program. The data that has been assembled to date suggest that the class (in general) is not as hazardous as the hydrazine-based fuels that are currently standard in hypergolic propulsion systems (Bausum and Johnson, 2006). However, much of the data for individual candidates has been estimated, and due to a paucity of relevant measured values in the open literature (and the EQT program's limited ability to obtain them otherwise), some estimates are based on methods that are not well validated. As discussed in a report summarizing a prior EQT-sponsored study to establish physical property data for the class (McQuaid, 2008), estimates for Henry's law constants are among this group.

Representing an expectation for the ratio of a compound's concentrations that will exist in the two phases of a ternary compound-air-water mixture at equilibrium, a compound's Henry's law constant is employed to predict its partitioning between air and water in the environment. Expressible in various ways, the values of the constants that are presented in this report are defined per

$$\text{HLC}(T) = RT[c_{\text{air}}(T)/c_{\text{water}}(T)], \quad (1)$$

where R is the universal gas constant (8.23×10^{-5} atm-m³/mole·K), T is the temperature (in K), $c_{\text{air}}(T)$ is the concentration of the compound in the mixture's gaseous phase, and $c_{\text{water}}(T)$ is the concentration of the compound in the mixture's aqueous phase. In addition, for environmental risk assessment, it is typical to seek and/or establish HLC(T) values for mixtures at 298 K and 1 atmosphere (atm), and HLC(T) values at that temperature and pressure are the only ones considered here.

In the aforementioned EQT-sponsored study, an attempt was made to establish the reliability of a quantitative structure property relationship's (QSPR's) HLC(298) estimates for EAs.

Implemented by the Environmental Protection Agency's (EPA's) HENRYWIN program (HENRYWIN, 2003), the QSPR is a bond contribution model, and it has a coefficient that was specifically developed for azide groups. It was surmised that the coefficient was derived from a measured HLC(298) value for hydrazoic acid (HN_3) (McQuaid, 2008), but the only check that was able to be made of the QSPR's validity for EAs was a comparison of its estimate for 2-azido-N,N-dimethylethanamine (DMAZ) to a value derived from "separately measured" values for DMAZ's vapor pressure [$\text{VP}(T)$] and water solubility [$\text{WS}(T)$] at 298 K,

$$\text{HLC(298)} \sim \text{VP(298)}/\text{WS(298)}. \quad (2)$$

(That is, the value was derived from [1] a VP(298) value measured above neat liquid DMAZ [Dee, 2000] and [2] a separate WS(298) measurement [Manzara, 2007], not the measured concentrations of DMAZ in the two phases of a ternary DMAZ-air-water mixture at equilibrium.) The value found via the equation 2 approximation (9.7×10^{-6} atm-m³/mol) is almost 2 orders of magnitude higher than the HENRYWIN estimate (1.2×10^{-7} atm-m³/mol).

Since the identification of an HLC(298) estimation method whose predictions for EAs could be trusted to be within an order of magnitude of actual values was desired, the aforementioned comparison was not encouraging. However, two other considerations suggested that the QSPR's estimate for DMAZ might be reasonable. The first was that an HLC(298) value for HN₃ derived from equation 2 with a measured WS(298) value and a trusted VP(298) estimate was also 2 orders of magnitude higher than a "true" HLC(298) measurement for the compound. Thus, it could be imagined that the HLC(298) estimate derived for DMAZ from equation 2 was too high, a speculation being that hydrogen bonding between gas-phase water molecules and DMAZ's lone pair sites leads to a lower DMAZ concentration above water than one would expect on the basis of its concentration above its neat liquid form. (A DMAZ molecule has hydrogen-bond accepting lone pair sites that allow it to hydrogen bond with water, but it does not have a hydrogen-bond donating site that allows it to hydrogen bond to another DMAZ molecule.)

Secondly, HENRYWIN's HLC(298) estimate for DMAZ could be rationalized on the basis of its comparison to a relatively well-validated estimate for N,N,N',N'-tetramethylethylenediamine [TMEDA, (CH₃)₂NCH₂CH₂N(CH₃)₂, 2.4×10^{-8} atm-m³/mol]. Both DMAZ and TMEDA can be thought of as N,N-dimethylethanamine with a functional group at the 2-position of the ethyl chain; in DMAZ's case the functional group being an azide, and in TMEDA's case the functional group being a dimethylamino fragment. Therefore, one can predict with some confidence the relative differences in their VP(298) and WS(298) values and, by extension, their HLC(298) values. TMEDA and DMAZ have similar VP(293) values; i.e., 10 mm Hg (Acros Organics, 1996) vs. 8 mm Hg (Dee, 2000), which is an observation one would predict on the basis of their molecules having similar molecular weights and little potential for strong attractive interactions (such as hydrogen bonding) with another of their own kind. But TMEDA's (second) dimethylamino fragment can bond more strongly to water than DMAZ's azide group can, which leads to the expectation that TMEDA will have a higher WS(298) than DMAZ. A value for DMAZ's WS(298) that was derived from measurements reported by Manzara (2007) indicates that it is $\sim 1.7 \times 10^5$ mg/L while TMEDA's WS(298) is estimated to be " 1×10^6 mg/L" (McQuaid, 2008). (A compound with a WS(298) value of 1×10^6 mg/L in essence means that it is miscible with water in all proportions.) Thus, while quantitative predictions based on these observations are not strongly defensible, the prediction that DMAZ's HLC(298) would be a factor of 5 higher value than TMEDA's seemed reasonable. Thus, HENRYWIN's estimates for EA candidates were considered adequate for the purpose of risk assessment for the stage of the selection process that existed at the time, and they were reported (McQuaid, 2008).

This report considers HLC(298) estimates for several EA candidates that were obtained by an alternate method. Investigated after the completion of the prior study, the method is based on calculating standard-state (298 K and 1 atm) gas- and aqueous-phase Gibbs free energies: G_g^o (298) and G_{aq}^o (298), respectively, from results obtained with a density functional theory/polarizable continuum model (DFT/PCM). From G_g^o (298) and G_{aq}^o (298), one can compute a compound's standard-state Gibbs free energy of solvation [ΔG_{sol}^o (298)],

$$\Delta G_{sol}^o(298) = G_{aq}^o(298) - G_g^o(298), \quad (3)$$

and it is related to a compound's HLC(298) per

$$HLC(298) = (R * 298) \exp[\Delta G_{sol}^o(298)/(R * 298)]. \quad (4)$$

Having more bona fide theoretical foundations than HENRYWIN's QSPR, DFT/PCM-based methods can in certain cases be a preferable option for generating HLC(298) estimates. However, for compounds whose molecules have a relatively large number of atoms, and thus a relatively large number of molecular conformations that need to be characterized in order to compute ΔG_{sol}^o (298), the method is far more expensive to implement than a QSPR. Moreover, such methods have their own potential pitfalls, and their results should be validated. (Each 1-kcal/mol error in a ΔG_{sol}^o (298) calculation will produce over a factor-of-5 error in the HLC(298) estimate, and errors of such magnitude are about the smallest one can hope to achieve with such methods.) But the lack of relevant measured values needed to validate EA HLC(298) estimates has already been noted. Thus, no attempt was made to employ such a method for the prior study. However, DFT/PCM results generated for a recently completed study of the aqueous-phase dissociation constants (K_a) of the conjugate acids of DMAZ, 2-azido-N-methylathanamine (MMAZ), 1-(2-azidoethyl)pyrrolidine (PyrrAZ), and 4-(2-azidoethyl)-morpholine (MorphAZ) (Stevenson and McQuaid, 2009) presented a low-risk, low-cost opportunity to obtain DFT/PCM-based HLC(298) estimates for them, and it was taken.

This report describes the DFT/PCM-based method employed to derive HLC(298) estimates and presents the method's estimates for DMAZ, MMAZ, PyrrAZ, MorphAZ, dimethylamine (DMA), trimethylamine (TMA), and 1-methylpyrrolidine (MP). (The chemical structures of the EAs are depicted in figure 1.) Inferences that can be drawn from a comparison of the estimates to values obtained by other means are discussed.

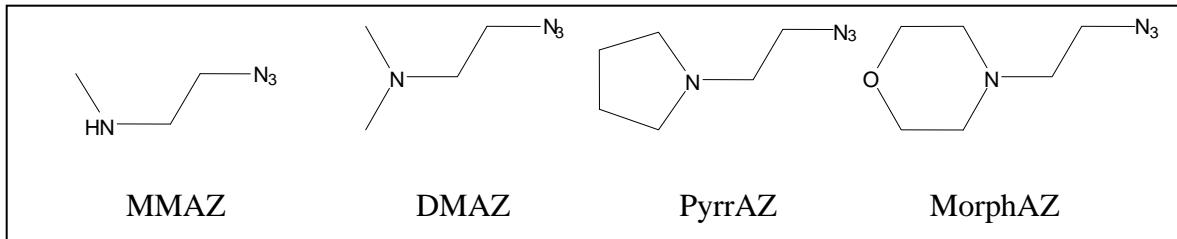


Figure 1. The chemical structures of EAs discussed in this report.

2. Computational Method

The theoretical method employed to calculate $G_g^o(298)$ and $G_{aq}^o(298)$ values—and from them $\Delta G_{sol}^o(298)$ and HLC(298)—is based on calculating gas- and aqueous-phase Gibbs free energies for equilibrium conformers of molecules of the compound of interest. Denoted for a given conformer (i) as $G_g(298,i)$ and $G_{aq}(298,i)$, respectively, figure 2 depicts the relationship between these two parameters and their reference state, which for a given molecule is the conformer (hereafter designated by the symbol X) with the lowest $G_g(298,i)$ value. $G_{aq}(298,i)$ and $G_g(298,X)$ are connected by the relationship

$$G_{aq}(298,i) = G_g(298,X) + \Delta G_g(298,i) + \Delta E'_g(i) + \Delta G_{sol}(298,i), \quad (5)$$

where (1) $\Delta G_g(298,i)$ is the difference between the free energy of the gas-phase equilibrium conformer whose geometry most closely resembles the aqueous-phase conformer and the free energy of the lowest-energy gas-phase conformer [$G_g(298,i) - G_g(298,X)$], (2) $\Delta E'_g(i)$ is the difference between the gas-phase electronic energy of the conformer's aqueous-phase geometry and the electronic energy of the gas-phase conformer whose geometry it most closely resembles, and (3) $\Delta G_{sol}(298,i)$ is the free energy change of solvation for the aqueous-phase geometry.

$G_g(298,i)$ is computed from

$$G_g(298,i) = E_g(i) + ZPVE_g(i) + \Delta G_g^{corr}(298,i), \quad (6)$$

where $E_g(i)$ is the conformer's electronic energy at 0 K, $ZPVE_g(i)$ is its zero-point vibrational energy, and $\Delta G_g^{corr}(298,i)$ is its “PV-TS” energy at 298 K, where P , V , and S are pressure, volume, and entropy, respectively.

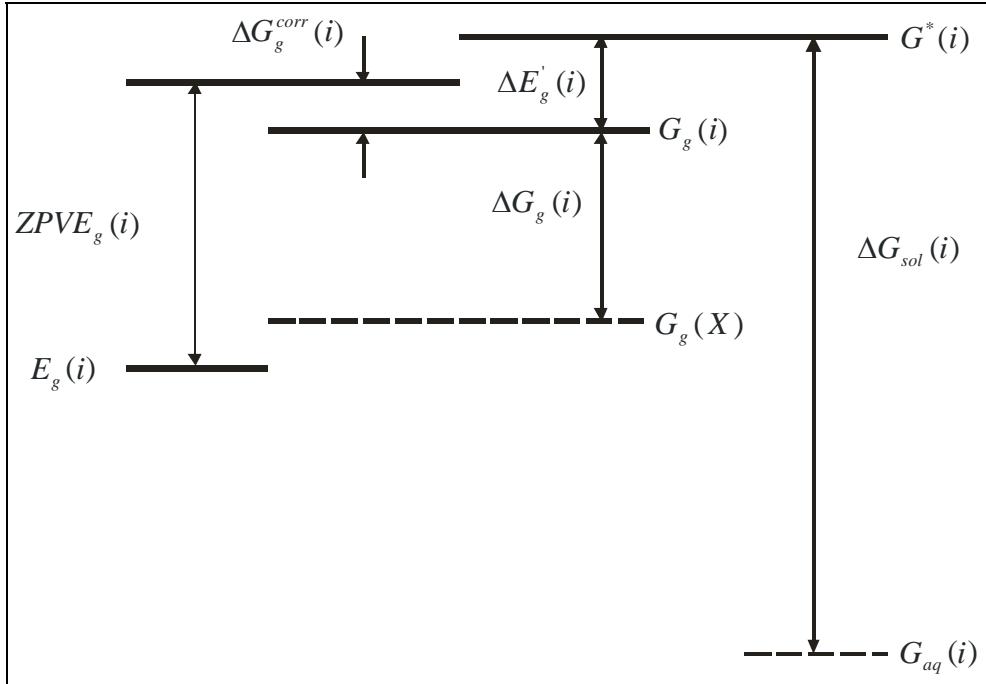


Figure 2. Relationships between defined thermodynamic parameters.

Values for the parameters defined in the preceding paragraph were derived from a slightly modified version of a procedure outlined by Saracino et al. (2003) and calculations performed with the Gaussian 03 (G03) suite of quantum chemistry codes (Frisch et al., 2003). Geometry optimizations were performed to identify the equilibrium structures that the molecules of interest would acquire in an aqueous environment. A PBE/PBEPBE/6-31+G(d,p) model (Perdew et al., 1996, 1997; Petersson et al., 1988; Clark et al., 1983) coupled with the PCM developed by Cossi et al. (2002) was employed for these optimizations. The optimizations' convergence criteria were maximum force ≤ 0.000450 hartree/bohr, root mean square (RMS) force ≤ 0.000300 hartree/bohr, maximum displacement ≤ 0.001800 bohr, and RMS displacement ≤ 0.001200 bohr. In accordance with the procedure outlined by Saracino et al., each structure's $\Delta G_{sol}(298,i)$ value was determined from the difference between its HF/6-31+G(d,p)-calculated gas- and (PCM-simulated) aqueous-phase single point electronic energies. “UAHF” radii were specified for the PCM calculations (Barone et al., 1997).

The geometries of the equilibrium structures found with the PCM-mediated PBEPBE/6-31+G(d,p) model were subsequently employed as starting points for gas-phase PBEPBE/6-31+G(d,p) geometry optimizations. The same convergence criteria as those employed for the PCM-mediated optimizations were employed for these optimizations. For all structures so obtained, normal mode analyses were conducted, and $ZPVE_g(i)$ and $\Delta G_g^{corr}(298,i)$ values were derived from them. G03's calculations of $\Delta G_g^{corr}(298,i)$ are based on the ideal gas law and the calculation of S via a standard method (McQuarrie, 1999).

An issue in the calculation of $\Delta G_g^{corr}(298,i)$ that was considered is the fact that many of the molecules characterized have low-frequency vibrational modes whose energy levels (and therefore $-TS$ contributions to the free energy) are more properly described by hindered internal rotation formulae than by harmonic oscillator formulae. Therefore, the G03 option for applying the more appropriate formulae was attempted for all cases. However, the method failed for all the ring-containing structures. The default G03 method, which is to treat all vibrational modes as harmonic oscillators, was therefore employed for these cases. It was assumed that the difference in the results produced by the two procedures would be small, and that expectation was met in the (only) case examined to test the assumption. The case was DMAZ, and for all the conformers that have been identified for it, the default calculation and the hindered rotor option yielded $\Delta G_g^{corr}(298,i)$ values that were identical to 10^{-6} hartrees. Therefore, this matter was not further considered.

It should also be noted that some of the gas-phase geometry optimizations produced structures that were not geometrically analogous to the aqueous-phase equilibrium geometries from which the optimizations were started. Regardless of the reason, if a gas-phase geometry optimization bypassed a local minimum that closely resembles the aqueous-phase geometry (starting point) and ended in a lower energy minimum that does not, the sum of $\Delta G_g(298,i)$ and $\Delta E_g'(i)$ that is obtained is still the same as it would be had the “optimal” local minimum been found. Only the relative contributions of the two parameters to the total are different. Thus, from the standpoint of having the potential to be sources of error in the calculation of the observable, such cases are not a concern.

To complete the calculation of parameters employed to compute $G_{aq}(298,i)$ values, gas-phase PBEPBE/6-311+G(2d,2p) single point energies for the gas- and PCM-mediated PBEPBE/6-31+G(d,p)-determined geometries were obtained. For each conformer, $\Delta E_g'(i)$ was computed from the difference between the two results, and the result for the gas-phase structure was added to the structure’s (unscaled) $ZPVE_g(i)$ and $\Delta G_g^{corr}(298,i)$ values to obtain $G_g(298,i)$ values, and from them $\Delta G_g(298,i)$ values. The $G_{aq}(298,i)$ values were obtained by adding $\Delta G_g(298,i)$, $\Delta E_g'(i)$, and $\Delta G_{sol}(298,i)$.

To compute $G_g^o(298)$ and $G_{aq}^o(298)$ for a molecule’s ensemble of conformers, it was assumed that the relative populations of the conformers in each phase would conform to a Boltzmann distribution,

$$P_{aq/g}(298,i) = \frac{g(i)\exp(-\Delta G_{aq/g}(298,i)/R*298)}{\sum_i g(i)\exp(-\Delta G_{aq/g}(298,i)/R*298)}, \quad (7)$$

where $g(i)$ is conformer i 's degeneracy factor. $G_g^o(298)$ and $G_{aq}^o(298)$ were then calculated by weighting the sums of $G_g(298,i)$ and $G_{aq}(298,i)$ in accordance with those distributions, i.e.,

$$G_{aq/g}^o(298) = \sum_i P_{aq/g}(298,i) G_{aq/g}(298,i). \quad (8)$$

In the implementation of equation 7, all conformers of all molecules were assumed to have C_1 symmetry and therefore assigned a $g(i)$ value equal to 1.

3. Results and Discussion

Table 1 lists the DFT/PCM-based $\Delta G_{sol}^o(298)$ and HLC(298) estimates that were obtained for DMA, TMA, MP, DMAZ, MMAZ, PyrrAZ, and MorphAZ, and it compares the HLC(298) estimates to values obtained by other means. The DFT/PCM results employed as input for the calculations are given in the appendix.

Table 1. Measured and estimated HLC(298) values for various amines.

Compound	$\Delta^0 G_{sol}$	HLC(298)	HLC(298)	HLC(298)
	DFT/PCM		HENRYWIN	Measured
	(kcal/mol)	(atm·m ³ /mol)	(atm·m ³ /mol)	(atm·m ³ /mol)
DMA ^a	-5.3	3.8×10^{-6}	1.7×10^{-5}	1.8×10^{-5}
TMA ^a	-3.5	6.6×10^{-5}	3.6×10^{-5}	1×10^{-4}
MP ^b	-4.5	1.2×10^{-5}	2.8×10^{-5}	3×10^{-5}
DMAZ	-7.6	6.4×10^{-8}	1.2×10^{-7}	—
MMAZ	-10.2	2.9×10^{-10}	5.3×10^{-8}	—
PyrrAZ	-9.2	4.3×10^{-9}	9.1×10^{-8}	—
MorphAZ	-13.2	5.1×10^{-12}	8.0×10^{-10}	—

^aChristie and Crisp (1967)

^bCabani et al. (1971)

Because measured HLC(298) values were found for DMA, TMA, and MP, the results for these cases represent a test of the reliability of the DFT/PCM-based method. (The measured values were in the training set from which HENRYWIN's QSPR was derived, so they do not constitute validating data for it.) The DFT/PCM-based HLC(298) estimate for DMA (3.8×10^{-6} atm·m³/mol) is a little less than a factor of 5 lower than the identified measured value (1.8×10^{-5} atm·m³/mol), the DFT/PCM-based HLC(298) estimate for TMA (6.6×10^{-5} atm·m³/mol) is a little less than a factor of 2 lower than the identified measured value (1×10^{-4} atm·m³/mol), and the DFT/PCM-based HLC(298) estimate for MP (1.2×10^{-5} atm·m³/mol) is a little over a factor of 2 lower than the identified measured value (3×10^{-5} atm·m³/mol). Combined, the results for DMA, TMA, and MP suggest that the DFT/PCM method is valid for aliphatic amines, but that its predictions for compounds in the class will be somewhat low.

The DFT/PCM-based HLC(298) estimate for DMAZ (6.4×10^{-8} atm·m³/mol) is about a factor of 2 smaller than the HENRYWIN estimate. As such, the result (coupled with the results for DMA, TMA, and MP) is considered support for (1) the contention that HENRYWIN's HLC(298) estimate for DMAZ is reasonable and (2) the suspicion that the HLC(298) value derived for DMAZ from VP(298) and WS(298) values is too high.

The DFT/PCM-based HLC(298) estimate for MMAZ (2.9×10^{-10} atm·m³/mol) is more than 2 orders of magnitude less than the HENRYWIN estimate (5.3×10^{-8} atm·m³/mol). Similarly, the DFT/PCM-based HLC(298) estimate for PyrrAZ (4.3×10^{-9} atm·m³/mol) is over an order of magnitude less than the HENRYWIN estimate (9.1×10^{-8} atm·m³/mol), and the DFT/PCM-based HLC(298) estimate for MorphAZ (5.1×10^{-12} atm·m³/mol) is over 2 orders of magnitude less than the HENRYWIN estimate (8×10^{-10} atm·m³/mol). Thus, one might conclude that the agreement between the two methods' estimates for these three compounds is poor. However, as has been noted, the volatilization from water of compounds with HLC(298) values below 3×10^{-7} atm·m³/mol is typically assumed to be negligible. Therefore, rather than being significantly different, the estimates from both the DFT/PCM-based method and HENRYWIN lead to this conclusion for these three compounds.

4. Summary

HLC(298) estimates for four EAs and three aliphatic amines were derived from a DFT/PCM-based method. The four EAs are 2-azido-N,N-dimethylethanamine (DMAZ), 2-azido-N-methylethanamine (MMAZ), 1-(2-azidoethyl)pyrrolidine (PyrrAZ), and 4-(2-azidoethyl)morpholine (MorphAZ), and the three aliphatic amines are dimethylamine (DMA), trimethylamine (TMA), and 1-methylpyrrolidine (MP). The DFT/PCM-based estimates for the three aliphatic amines indicate that the method's estimates for aliphatic amines will be within an order of magnitude of actual values, but somewhat low. The DFT/PCM-based HLC(298) estimate for DMAZ is about a factor of 2 smaller than the estimate obtained for it from the EPA's HENRYWIN program and thus supports the reasonableness of the HENRYWIN estimate. In percentage terms, the DFT/PCM-based HLC(298) estimates for MMAZ, PyrrAZ, and MorphAZ are all significantly lower than those obtained from HENRYWIN, but the estimates from both methods suggest that the volatilization of these compounds from water will be negligible. Taken together, the results from the DFT/PCM-based method support the conclusion of a previous study of HENRYWIN's HLC(298) predictions for EA candidates (McQuaid, 2008), i.e., that the predictions merit use as input for modeling such candidates' transport through the environment.

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Appendix. DFT/PCM Results for Various Amines

This appendix reproduces a subset of density functional theory/polarizable continuum model (DFT/PCM) results that were generated for a study that was performed to determine if the aqueous phase dissociation constants (K_a) of the conjugate acids of 2-azidoethanamines (EAs) correlated with features of the molecular structure of the acids or their corresponding bases. Included here are all the results that are needed to compute ΔG_{sol}^o (298) values for dimethylamine (DMA), trimethylamine (TMA), 1-methylpyrrolidine (MP), 2-azido-N,N-dimethyl ethanamine (DMAZ), 2-azido-N-methylethanamine (MMAZ), 1-(2-azidoethyl)-pyrrolidine (PyrrAZ), and 4-(2-azidoethyl)morpholine (MorphAZ). For DMA, TMA, and MP, only one conformer is important. The molecular structures of DMAZ's and MMAZ's conformers have been discussed in detail in prior reports,^{1,2} and their labels in the tables in this appendix correspond to the labels in those reports. The labels of the conformers of PyrrAZ and MorphAZ were assigned on the basis of their molecular structure, a given letter identifying a correspondence between the molecular geometry of a PyrrAZ or MorphAZ conformer and that of an MMAZ or DMAZ conformer with the same letter.

Table A-1. DFT/PCM results for DMA, TMA, and MP.

Compound	ΔG_{sol}^a (kcal/mol)	$E'(SCF)^b$ (hartrees)	$E(SCF)^c$ (hartrees)	ΔE_g^d (kcal/mol)	$\Delta^0 G_{sol}$ (kcal/mol)
DMA	-5.37	-135.020237	-135.020398	0.10	-5.27
TMA	-3.53	-174.281905	-174.281973	0.04	-3.49
MP	-4.59	-251.623022	-251.623115	0.11	-4.48

^aValue calculated for the conformer's PCM-mediated PBEPBE/6-31+G(d,p) optimized geometry.

^bPBEPBE/6-311+G(2d,2p) single point energy calculated for the PCM-mediated PBEPBE/6-31+G(d,p) optimized geometry.

^cPBEPBE/6-311+G(2d,2p) single point energy calculated for the gas-phase PBEPBE/6-31+G(d,p) optimized geometry.

^d $E'(SCF) - E(SCF)$.

¹McQuaid, M. J. *The Structure of Secondary 2-Azidoethanamines: A Hypergolic Fuel vs. a Nonhypergolic Fuel*; ARL-TR-3176; U.S. Army Research Laboratory: Aberdeen Proving Ground, MD, 2004.

²McQuaid, M. J.; McNesby, K. L.; Rice, B. M.; Chabalowski, C. F. Density Functional Theory Characterization of the Structure and Gas-Phase, Mid-Infrared Absorption Spectrum of 2-Azido-N,N-dimethylethanamine (DMAZ). *J. Mol. Struct. (THEOCHEM)* **2002**, 587, 199–218.

Table A-2. DFT/PCM results for DMAZ: gas phase.

Label	E'(SCF) ^a (hartrees)	E(SCF) ^b (hartrees)	ΔE^c (kcal/mol)	ZPVE + ΔG_{corr} (hartrees)	G_g (hartrees)	ΔG_g (kcal/mol)	Rel. Pop.
A	-377.026882	-377.027258	0.24	0.113168	-376.914090	0.5	0.10
B	-377.028564	-377.028763	0.12	0.113810	-376.914953	0.0	0.25
C	-377.026792	-377.026963	0.11	0.113516	-376.913447	0.9	0.05
D	-377.026620	-377.026849	0.14	0.112935	-376.913914	0.7	0.08
E	-377.027261	-377.027421	0.10	0.112617	-376.914804	0.1	0.22
F	-377.027225	-377.027356	0.08	0.113292	-376.914064	0.6	0.10
G	-377.027066	-377.027240	0.11	0.113032	-376.914208	0.5	0.12
H	-377.025334	-377.025546	0.13	0.113305	-376.912241	1.7	0.01
I	-377.025188	-377.025383	0.12	0.112667	-376.912716	1.4	0.02
J	-377.024796	-377.025100	0.19	0.112594	-376.912506	1.5	0.02
K	-377.024801	-377.025028	0.14	0.113205	-376.911823	2.0	0.01
L	-377.025245	-377.025455	0.13	0.113507	-376.911948	1.9	0.01
M	-377.026490	-377.028721	1.40	0.113993	-376.914953 ^d	—	—

^aPBEPBE/6-311+G (2d,2p) single point energy calculated for the conformer's PCM-mediated PBEPBE/6-31+G(d,p) optimized geometry.

^bPBEPBE/6-311+G(2d,2p) single point energy calculated for the gas-phase PBEPBE/6-31+G(d,p) optimized geometry.

^cE'(SCF) - E(SCF).

^dConformer M is an aqueous-phase structure that has no gas-phase analog. Gas-phase optimizations started from conformer M ended as conformer B.

Table A-3. DFT/PCM results for DMAZ: aqueous phase.

Label	ΔG_{sol}^a (kcal/mol)	G_{aq} (kcal/mol)	ΔG_{aq} (kcal/mol)	Rel. Pop.
A	-7.83	-7.05	0.7	0.12
B	-6.09	-5.97	1.7	0.02
C	-6.86	-5.81	1.9	0.02
D	-7.03	-6.23	1.5	0.03
E	-7.56	-7.37	0.3	0.21
F	-7.38	-6.74	1.0	0.07
G	-7.44	-6.86	0.8	0.09
H	-7.45	-5.61	2.1	0.01
I	-7.70	-6.17	1.5	0.03
J	-7.13	-5.40	2.3	0.01
K	-6.67	-4.56	3.1	0.00
L	-6.97	-4.95	2.8	0.00
M	-9.11	-7.71	0.0	0.38

^aValue calculated for the conformer's PCM-mediated PBEPBE/6-31+G(d,p) optimized geometry.

Table A-4. DFT/PCM results for MMAZ: gas phase.

Label	E'(SCF) ^a (hartrees)	E(SCF) ^b (hartrees)	ΔE ^c (kcal/mol)	ZPVE+ΔG ^{corr} (hartrees)	G _g (hartrees)	ΔG _g (kcal/mol)	Rel. Pop.
A1	-337.766635	-337.766999	0.23	0.087913	-337.679086	1.9	0.02
B1	-337.768361	-337.768632	0.17	0.088562	-337.680070	1.2	0.04
C1	-337.769138	-337.769566	0.27	0.088267	-337.681299	0.5	0.16
D1	-337.76988	-337.770222	0.21	0.088183	-337.682039	0.0	0.35
E1	-337.767703	-337.767918	0.13	0.087767	-337.680151	1.2	0.05
F1	-337.767613	-337.767813	0.13	0.088031	-337.679782	1.4	0.03
G1	-337.767475	-337.767697	0.14	0.088021	-337.679676	1.5	0.03
H1	-337.766140	-337.766379	0.15	0.088038	-337.678341	2.3	0.01
I1	-337.765955	-337.766183	0.14	0.087350	-337.678833	2.0	0.01
J1	-337.768213	-337.768454	0.15	0.087659	-337.680795	0.8	0.09
K1	-337.767536	-337.767749	0.13	0.088607	-337.679142	1.8	0.02
L1	-337.767361	-337.767609	0.16	0.087901	-337.679708	1.5	0.03
M1	-337.766406	-337.768642	1.40	0.088598	-337.680044 ^d	—	—
A2	-337.766142	-337.766437	0.19	0.088331	-337.678106	2.5	0.01
B2	-337.768022	-337.768331	0.19	0.088391	-337.679940	1.3	0.04
C2	-337.766403	-337.766632	0.14	0.088425	-337.678207	2.4	0.01
D2	-337.766414	-337.766694	0.18	0.087738	-337.678956	1.9	0.01
E2	-337.767048	-337.767278	0.14	0.087450	-337.679828	1.4	0.03
F2	-337.766951	-337.767185	0.15	0.088001	-337.679184	1.8	0.02
G2	-337.766828	-337.767048	0.14	0.087965	-337.679083	1.9	0.02
H2	-337.766048	-337.766290	0.15	0.087966	-337.678324	2.3	0.01
J2	-337.764928	-337.765226	0.19	0.087378	-337.677848	2.6	0.00
K2	-337.764766	-337.765033	0.17	0.087842	-337.677191	3.0	0.00
L2	-337.765305	-337.765580	0.17	0.088199	-337.677381	2.9	0.00
M2	-337.765940	-337.768336	1.50	0.088470	-337.679866 ^e	—	—
X2	-337.766289	-337.766525	0.15	0.087794	-337.678731	2.1	0.01

^aPBEPBE/6-311+G(2d,2p) single point energy calculated for the conformer's PCM-mediated PBEPBE/6-31+G(d,p) optimized geometry.

^bPBEPBE/6-311+G(2d,2p) single point energy calculated for the gas-phase PBEPBE/6-31+G(d,p) optimized geometry.

^cE'(SCF) - E(SCF).

^dConformer M1 is an aqueous-phase structure that has no gas-phase analog. Gas-phase optimizations started from conformer M1 ended as conformer B1.

^eConformer M2 is an aqueous-phase structure that has no gas-phase analog. Gas-phase optimizations started from conformer M2 ended as conformer B2.

Table A-5. DFT/PCM results for MMAZ: aqueous phase.

Label	ΔG_{sol}^a (kcal/mol)	G_{aq} (kcal/mol)	ΔG_{aq} (kcal/mol)	Rel. Pop.
A1	-10.38	-8.3	1.8	0.02
B1	-9.17	-7.8	2.4	0.01
C1	-9.23	-8.5	1.6	0.03
D1	-8.86	-8.6	1.5	0.04
E1	-9.79	-8.5	1.7	0.03
F1	-9.77	-8.2	1.9	0.02
G1	-9.67	-8.0	2.1	0.02
H1	-10.05	-7.6	2.5	0.01
I1	-10.13	-8.0	2.2	0.01
J1	-9.13	-8.2	1.9	0.02
K1	-9.00	-7.0	3.1	0.00
L1	-9.44	-7.8	2.3	0.01
M1	-11.53	-10.1	0.0	0.53
A2	-10.04	-7.4	2.7	0.01
B2	-8.79	-7.3	2.8	0.00
C2	-8.98	-6.4	3.7	0.00
D2	-8.94	-6.8	3.3	0.00
E2	-9.52	-8.0	2.1	0.01
F2	-9.39	-7.5	2.7	0.01
G2	-9.48	-7.5	2.6	0.01
H2	-9.91	-7.4	2.7	0.01
J2	-9.53	-6.7	3.4	0.00
K2	-9.20	-6.0	4.1	0.00
L2	-9.34	-6.2	3.9	0.00
M2	-11.01	-9.5	0.6	0.19
X2	-8.47	-6.2	3.9	0.00

^aValue calculated for the conformer's PCM-mediated PBEPBE /6-31+G(d,p) optimized geometry.

Table A-6. DFT/PCM results for PyrrAZ: gas phase.

Label	E'(SCF) ^a (hartrees)	E(SCF) ^b (hartrees)	ΔE ^c (kcal/mol)	ZPVE + ΔG _{corr} (hartrees)	G _g (hartrees)	ΔG _g (kcal/mol)	Rel. Pop.
A	-454.368672	-454.369013	0.21	0.146784	-454.222229	0.67	0.08
B	-454.370402	-454.370566	0.10	0.147266	-454.223300	0.00	0.24
C	-454.368870	-454.369020	0.09	0.147070	-454.221950	0.85	0.06
D	-454.368702	-454.368884	0.11	0.146668	-454.222216	0.68	0.08
E	-454.369200	-454.369322	0.08	0.146252	-454.223070	0.14	0.19
F	-454.369121	-454.369240	0.07	0.146809	-454.222431	0.55	0.10
G	-454.368996	-454.369121	0.08	0.146742	-454.222379	0.58	0.09
H	-454.365945	-454.366099	0.10	0.146643	-454.219456	2.41	0.00
I	-454.365807	-454.365960	0.10	0.145899	-454.220061	2.03	0.01
J	-454.365496	-454.365709	0.13	0.145378	-454.220331	1.86	0.01
K	-454.365329	-454.365466	0.09	0.146219	-454.219247	2.54	0.00
L	-454.365919	-454.366088	0.11	0.146644	-454.219444	2.42	0.00
M	-454.368351	-454.368571	0.14	0.145866	-454.222705	0.37	0.13
A1	-454.363064	-454.363474	0.26	0.146238	-454.217236	3.80	0.00
B1	-454.365580	-454.365773	0.12	0.147418	-454.218355	3.10	0.00
C1	-454.363484	-454.363673	0.12	0.147328	-454.216345	4.36	0.00
D1	-454.363938	-454.364137	0.12	0.148302	-454.215835	4.68	0.00
E1	-454.364485	-454.364662	0.11	0.146523	-454.218139	3.24	0.00
F1	-454.364457	-454.364580	0.08	0.146978	-454.217602	3.58	0.00
G1	-454.364391	-454.364533	0.09	0.147017	-454.217516	3.63	0.00
H1	-454.361856	-454.362043	0.12	0.147184	-454.214859	5.30	0.00
I1	-454.361581	-454.361746	0.10	0.146372	-454.215374	4.97	0.00
J1	-454.360743	-454.361401	0.41	0.146609	-454.214792	5.34	0.00
L1	-454.361066	-454.361260	0.12	0.147300	-454.213960	5.86	0.00
M1	-454.363159	-454.365789	1.65	0.147305	-454.218484 ^d	—	—

^aPBEPBE/6-311+G (2d,2p) single point energy calculated for the conformer's PCM-mediated PBEPBE/6-31+G(d,p) optimized geometry.

^bPBEPBE/6-311+G(2d,2p) single point energy calculated for the gas-phase PBEPBE/6-31+G(d,p) optimized geometry.

^cE'(SCF) - E(SCF).

^dConformer M1 is an aqueous-phase structure that has no gas-phase analog. Gas-phase optimizations started from conformer M1 ended as conformer B1.

Table A-7. DFT/PCM results for PyrrAZ: aqueous phase.

Label	ΔG_{sol}^a (kcal/mol)	G_{aq} (kcal/mol)	ΔG_{aq} (kcal/mol)	Rel. Pop.
A	-8.76	-7.9	1.4	0.06
B	-6.85	-6.7	2.6	0.01
C	-7.78	-6.8	2.5	0.01
D	-7.93	-7.1	2.2	0.02
E	-8.55	-8.3	1.0	0.12
F	-8.40	-7.8	1.5	0.05
G	-8.43	-7.8	1.5	0.05
H	-8.49	-6.0	3.3	0.00
I	-8.65	-6.5	2.8	0.01
J	-8.09	-6.1	3.2	0.00
K	-7.38	-4.8	4.6	0.00
L	-7.81	-5.3	4.0	0.00
M	-9.83	-9.3	0.0	0.66
A1	-10.06	-6.0	3.3	0.00
B1	-7.49	-4.3	5.1	0.00
C1	-8.12	-3.6	5.7	0.00
D1	-8.05	-3.2	6.1	0.00
E1	-8.92	-5.6	3.7	0.00
F1	-8.64	-5.0	4.3	0.00
G1	-8.82	-5.1	4.2	0.00
H1	-8.92	-3.5	5.8	0.00
I1	-9.15	-4.1	5.2	0.00
J1	-7.70	-1.9	7.4	0.00
L1	-7.45	-1.5	7.9	0.00
M1	-10.66	-6.0	3.3	0.00

^aValue calculated for the conformer's PCM-mediated PBEPBE /6-31+G(d,p) optimized geometry.

Table A-8. DFT/PCM results for MorphAZ: gas phase.

Label	E'(SCF) ^a (hartrees)	E(SCF) ^b (hartrees)	ΔE ^c (kcal/mol)	ZPVE + ΔG _{corr} (hartrees)	G _g (hartrees)	ΔG _g (kcal/mol)	Rel. Pop.
A	-529.532886	-529.533193	0.2	0.151273	-529.381920	0.6	0.11
B	-529.534570	-529.534774	0.1	0.152011	-529.382884	0.1	0.26
C	-529.532752	-529.532956	0.1	0.151793	-529.381163	1.1	0.05
D	-529.532625	-529.532882	0.2	0.151145	-529.381737	0.7	0.09
E	-529.533036	-529.533223	0.1	0.150741	-529.382482	0.3	0.19
F	-529.532920	-529.533107	0.1	0.151044	-529.382063	0.5	0.12
G	-529.532833	-529.533016	0.1	0.151144	-529.381872	0.6	0.10
H	-529.531035	-529.531242	0.1	0.151338	-529.379904	1.9	0.01
I	-529.530935	-529.531140	0.1	0.150700	-529.380440	1.5	0.02
J	-529.530547	-529.530833	0.2	0.150674	-529.380159	1.7	0.02
K	-529.530147	-529.530378	0.1	0.150379	-529.379999	1.8	0.01
L	-529.530905	-529.531105	0.1	0.151577	-529.379528	2.1	0.01
M	-529.532530	-529.534773	1.4	0.151889	-529.382884 ^d	—	—
A1	-529.526172	-529.526592	0.3	0.151008	-529.375584	4.6	0.00
B1	-529.528559	-529.528860	0.2	0.151958	-529.376902	3.8	0.00
C1	-529.526423	-529.526653	0.1	0.150994	-529.375659	4.5	0.00
D1	-529.526725	-529.526976	0.2	0.150993	-529.375983	4.3	0.00
E1	-529.527316	-529.527515	0.1	0.150968	-529.376547	4.0	0.00
F1	-529.527224	-529.527407	0.1	0.151385	-529.376022	4.3	0.00
G1	-529.527139	-529.527329	0.1	0.151341	-529.375988	4.3	0.00
H1	-529.525027	-529.525230	0.1	0.151455	-529.373775	5.7	0.00
I1	-529.524820	-529.525038	0.1	0.150653	-529.374385	5.3	0.00
J1	-529.524570	-529.524804	0.1	0.150977	-529.373827	5.7	0.00
L1	-529.524401	-529.524609	0.1	0.150790	-529.373819	5.7	0.00
M1	-529.526256	-529.528811	1.6	0.151591	-529.377220 ^e	—	—

^aPBEPBE/6-311+G (2d,2p) single point energy calculated for the conformer's PCM-mediated PBEPBE/6-31+G(d,p) optimized geometry.

^bPBEPBE/6-311+G(2d,2p) single point energy calculated for the gas-phase PBEPBE/6-31+G(d,p) optimized geometry.

^cE'(SCF) - E(SCF).

^dConformer M is an aqueous-phase structure that has no gas-phase analog. Gas-phase optimizations started from conformer M ended as conformer B.

^eConformer M1 is an aqueous-phase structure that has no gas-phase analog. Gas-phase optimizations started from conformer M1 ended as conformer B1.

Table A-9. DFT/PCM results for MorphAZ: aqueous phase.

Label	ΔG_{sol}^a (kcal/mol)	G_{aq} (kcal/mol)	ΔG_{aq} (kcal/mol)	Rel. Pop.
A	-13.09	-12.3	0.9	0.07
B	-11.68	-11.5	1.7	0.02
C	-12.24	-11.0	2.1	0.01
D	-12.44	-11.6	1.6	0.02
E	-13.42	-13.1	0.1	0.25
F	-13.33	-12.7	0.5	0.14
G	-13.31	-12.6	0.6	0.11
H	-13.43	-11.4	1.7	0.02
I	-13.5	-11.8	1.3	0.03
J	-12.78	-10.9	2.3	0.01
K	-12.28	-10.3	2.8	0.00
L	-12.81	-10.6	2.6	0.00
M	-14.58	-13.2	0.0	0.31
A1	-14.46	-9.6	3.6	0.00
B1	-12.29	-8.3	4.8	0.00
C1	-12.63	-8.0	5.2	0.00
D1	-12.63	-8.1	5.0	0.00
E1	-13.73	-9.6	3.5	0.00
F1	-13.52	-9.1	4.1	0.00
G1	-13.68	-9.2	3.9	0.00
H1	-13.44	-7.6	5.6	0.00
I1	-13.25	-7.8	5.4	0.00
J1	-11.80	-6.0	7.2	0.00
L1	-11.84	-6.0	7.2	0.00
M1	-15.32	-10.2	3.0	0.00

^aValue calculated for the conformer's PCM-mediated PBE/PBE
/6-31+G(d,p) optimized geometry.

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